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(54) Conversion of syngas into dimethyl ether

(57) Synthesis gas, optionally together with water, is contacted at 232 to 399°C with a catalyst comprising coprecipitated Cr, Cu and Zn components in which the atomic ratio Cr/(Cu+Zn) is 0.1 to 1.0 and an acidic dehydrating component and aged catalyst is regenerated by contact with an oxygen-containing gas at 38 to 538°C.

The drawings originally filed were informal and the prints here reproduced taken from later filed formal copies.
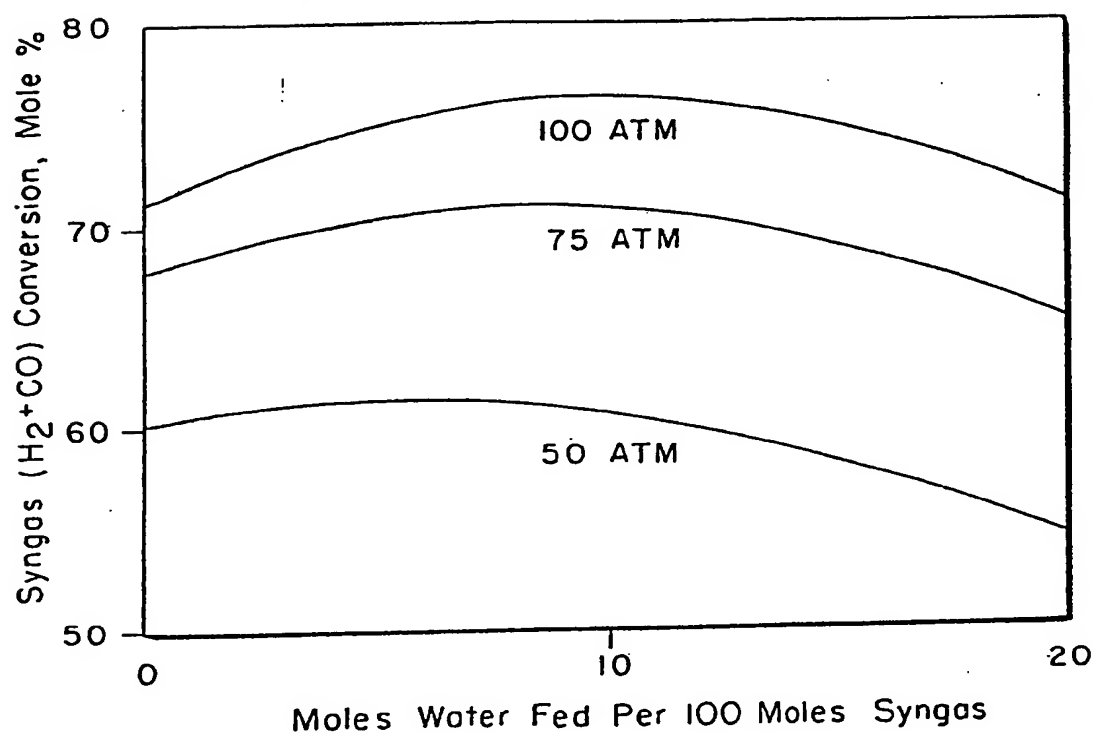
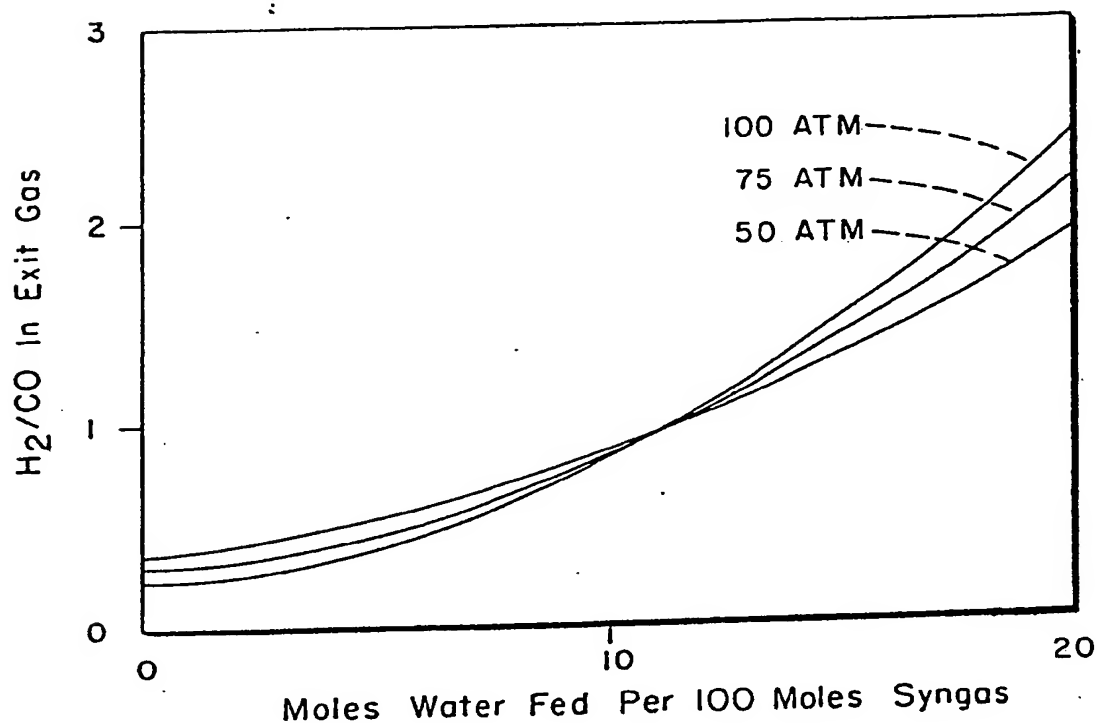## FIG. 1   EFFECT OF CO-FED WATER

Syngas (H_2+CO) Conversion, Mole %

100 ATM

75 ATM

50 ATM

Moles Water Fed Per 100 Moles Syngas

FIG. 2   EFFECT OF CO-FED WATER

H_2/CO In Exit Gas

100 ATM

75 ATM

50 ATM

Moles Water Fed Per 100 Moles Syngas

FIG. 3   TOTAL SYNGAS CONVERSION

Feed
H₂O/CO ● 0.0   ○ 0.04   ▯ 0.12   △ 0.25   ▽ 0.37
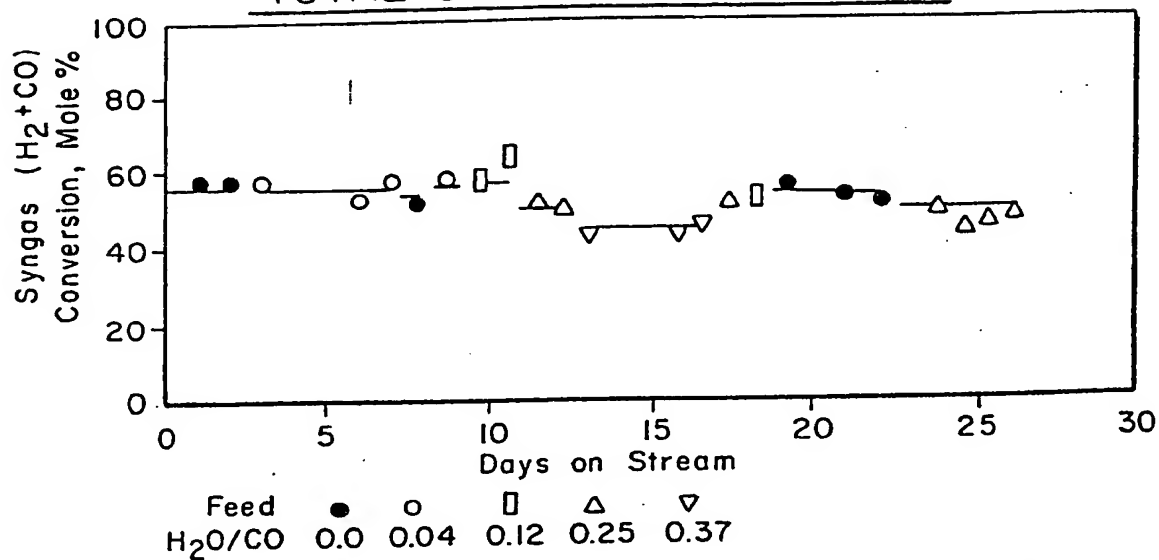
FIG. 4A   H₂/CO PRODUCT SELECTIVITY

TOTAL SYNGAS CONVERSION   FIG. 4B

SYNGAS $(H_2/CO<1)$

H_2O

DME SYNTH. 4

H_2, CO 10

F—T 18

HC CO_2, H_2O 20

LPG
Gasoline
Diesel Fuel

M 22

14

Gasoline 16

2

8

6

12

FIG. 5
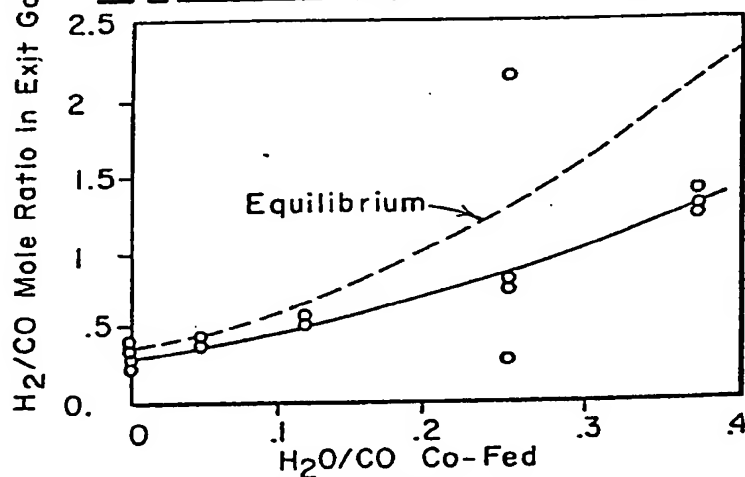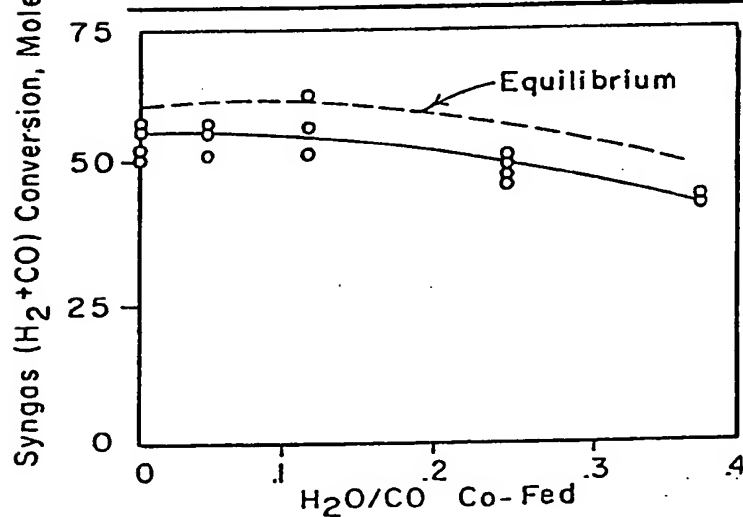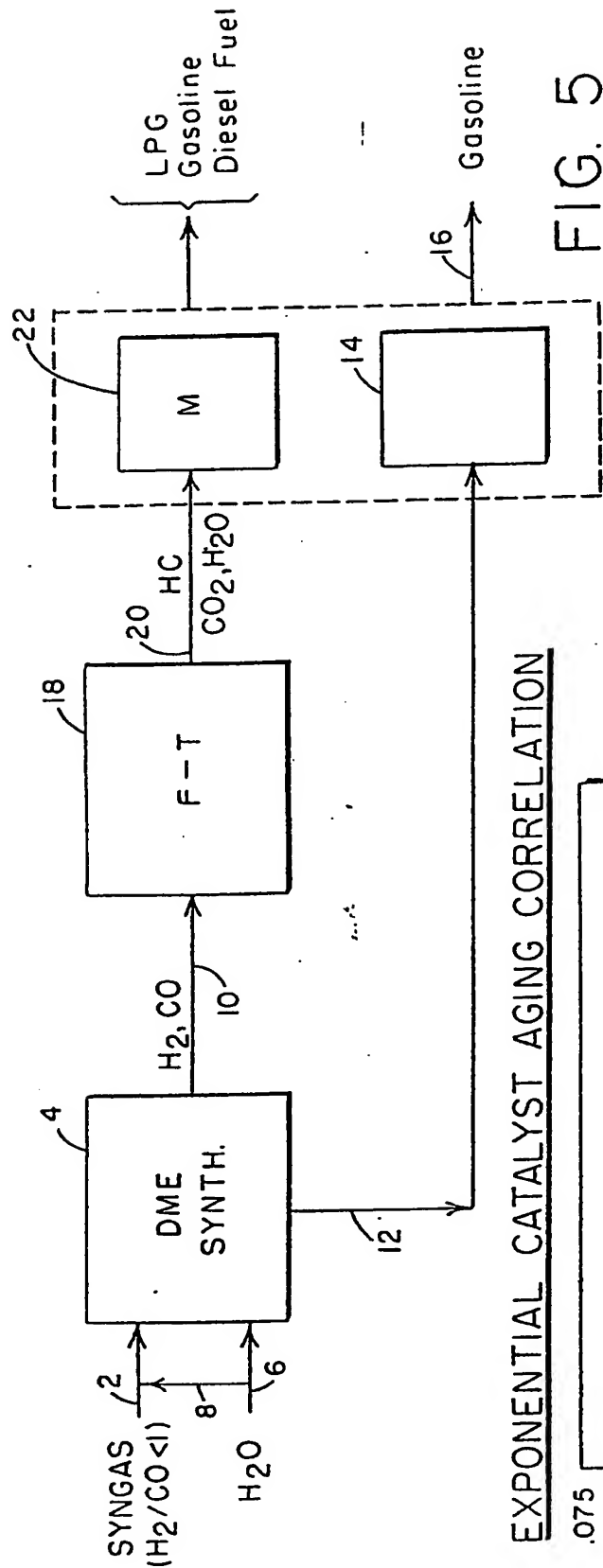
EXPONENTIAL CATALYST AGING CORRELATION
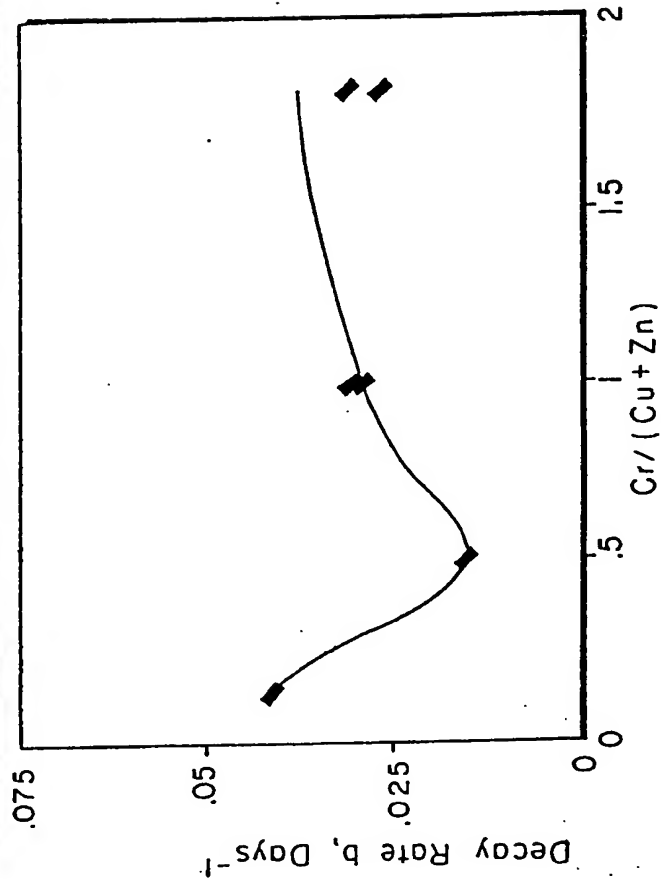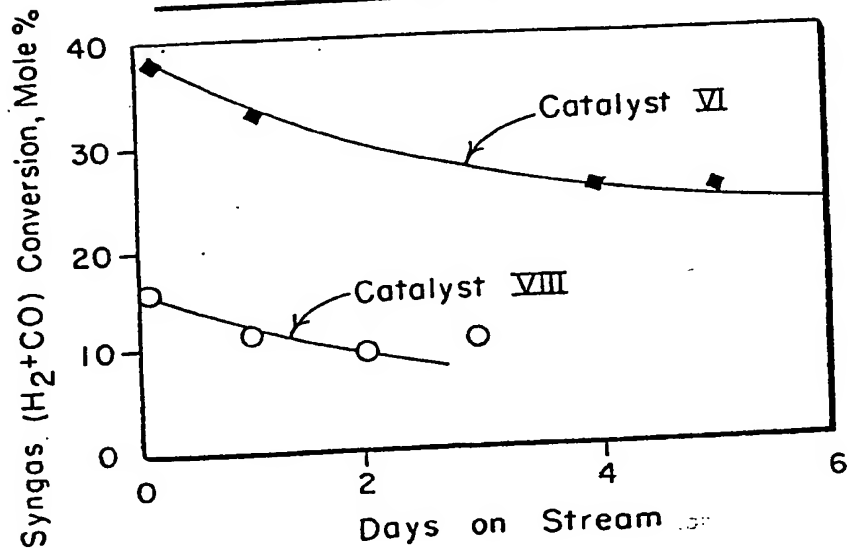
Decay Rate b, Days^{-1}

$Cr/(Cu+Zn)$

.075

.05

.025

0

.5

1

1.5

2

FIG. 6

FIG. 7

TOTAL SYNGAS CONVERSION

Syngas (H$_2$+CO) Conversion, Mole %

Catalyst VI

Catalyst VIII

Days on Stream

FIG. 8

TOTAL SYNGAS CONVERSION

Syngas (H$_2$+CO) Conversion, Mole %

Equilibrium

3rd Day

Daily

Regeneration

No

Daily

Regeneration

GHSV 4000

GHSV 2000

Days on Stream

FIG. 9

TOTAL SYNGAS CONVERSION

Solid points indicate oxidative regeneration followed the material balance

FIG. 10

TOTAL SYNGAS CONVERSION

Solid points indicate oxidative regeneration followed the material balance

FIG. 11

TOTAL SYNGAS CONVERSION

Catalyst X

Solid points indicate oxidative regeneration followed the material balance

FIG. 12

TOTAL SYNGAS CONVERSION

Catalyst XI

Solid points indicate oxidative regeneration followed the material balance

2097382

FIG. 13

TOTAL SYNGAS CONVERSION

Catalyst XII

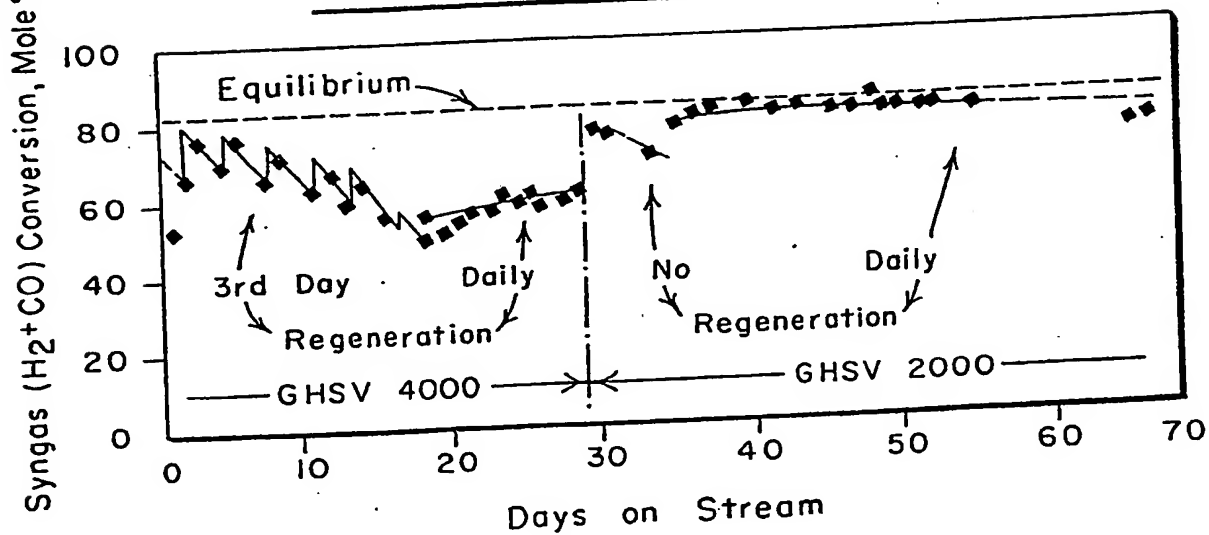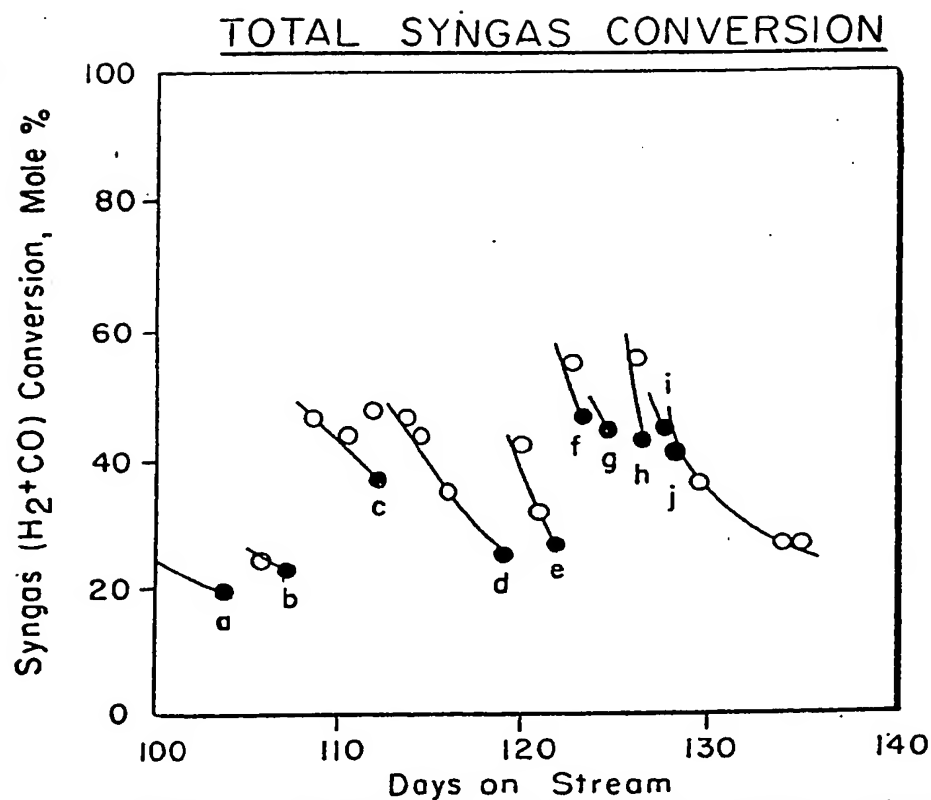Solid points indicate oxidative regeneration followed the material balance

FIG. 14

TOTAL SYNGAS CONVERSION

Catalyst XIII
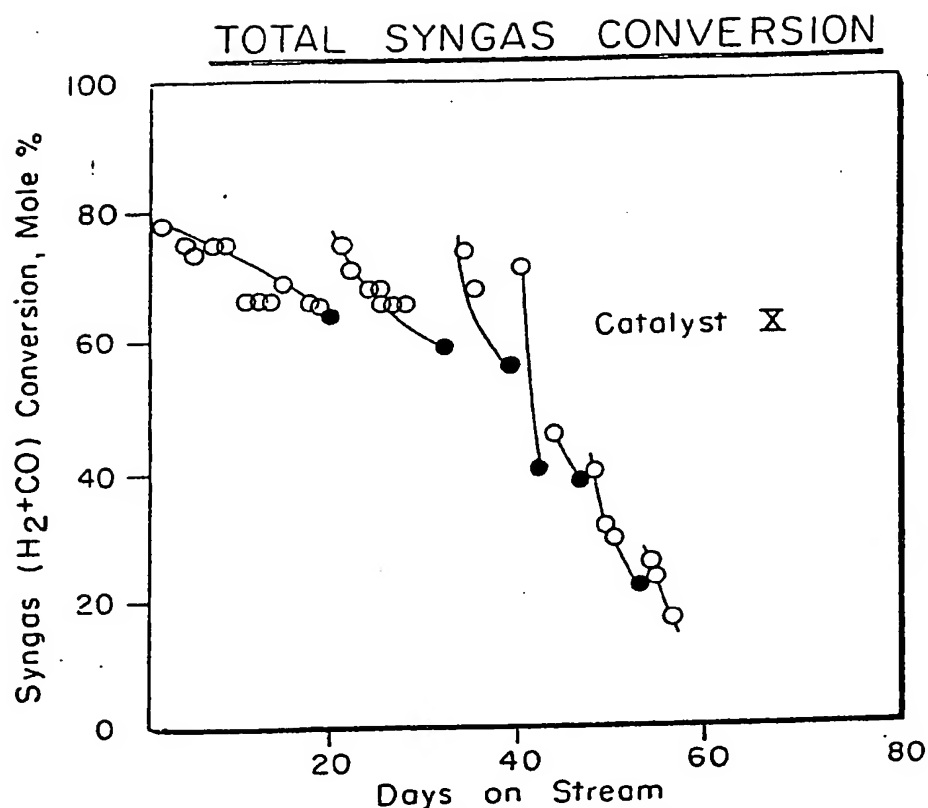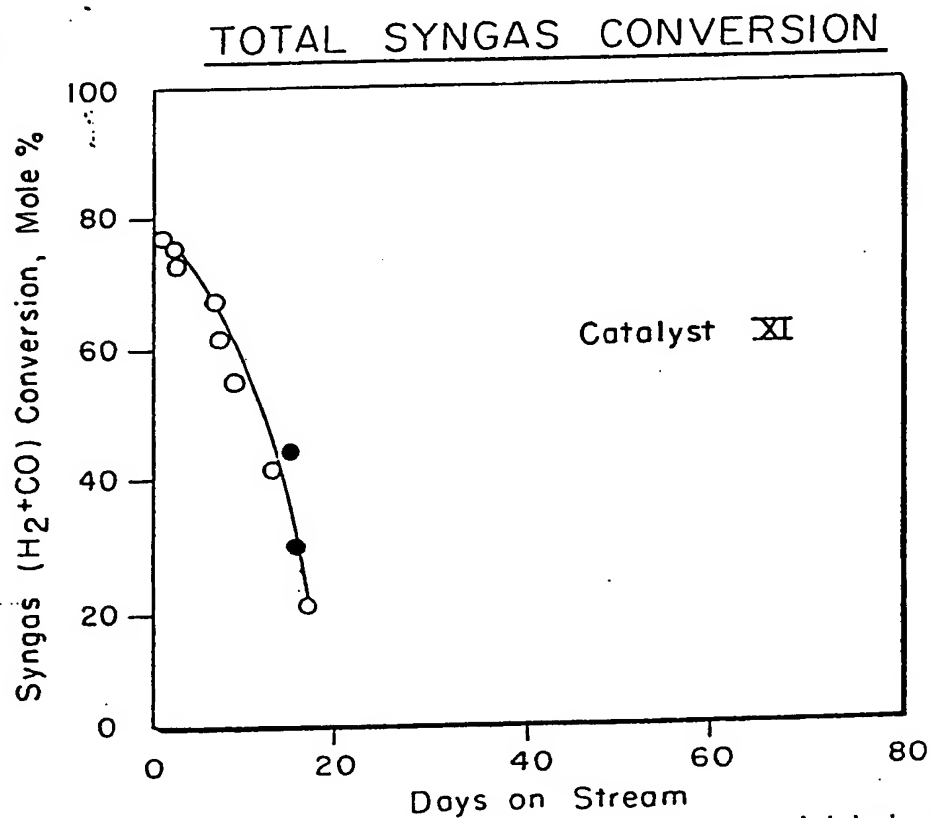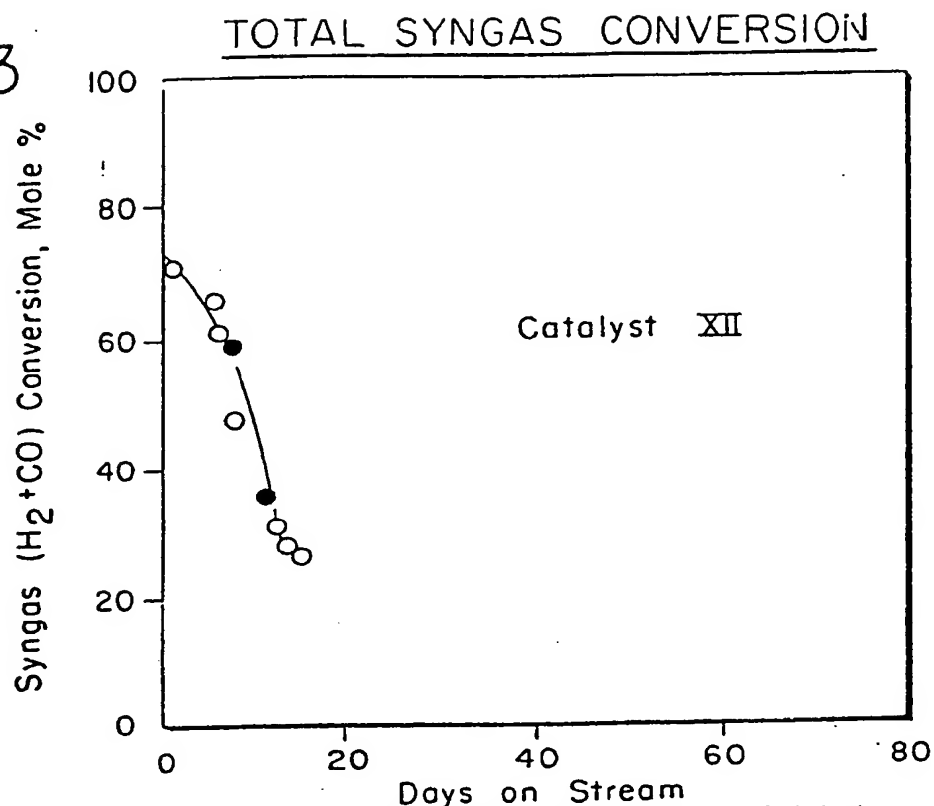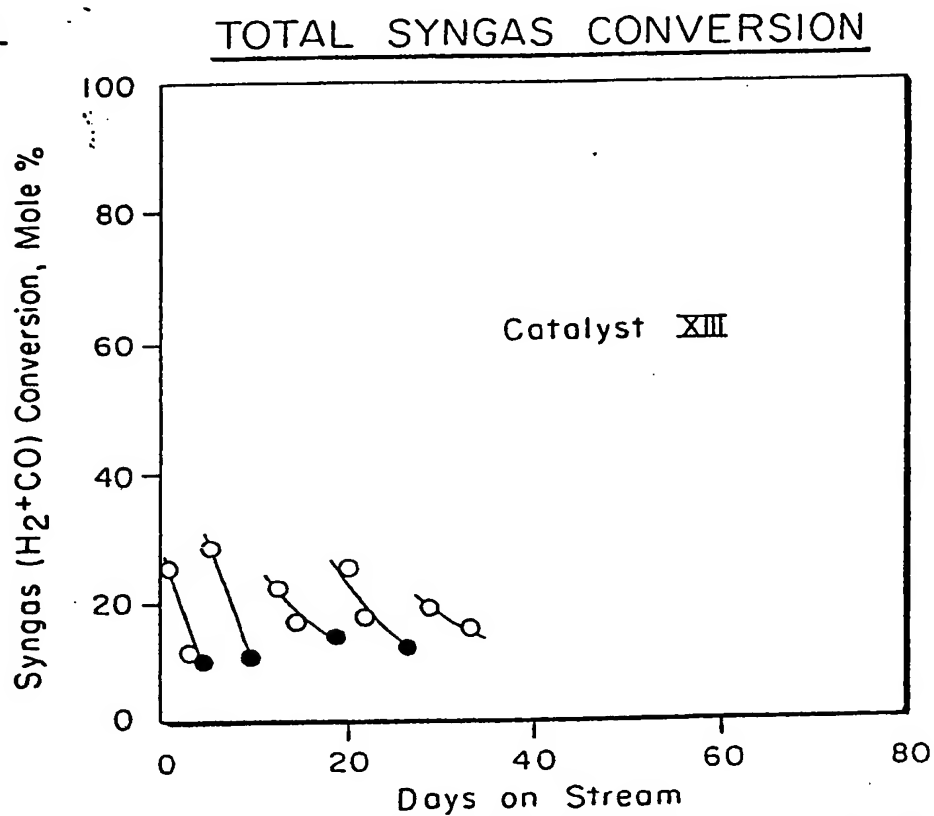
Solid points indicate oxidative regeneration followed the material balance

SPECIFICATION
Conversion of syngas into dimethyl ether

There are at present two major routes for effecting the conversion of coal via synthesis gas into liquid fuels, comprising the well publicized Fischer-Tropsch (F—T) process and a more recently
5 developed methanol-to-gasoline process such as that described in U.S. Patent 3,928,483. The Fischer-Tropsch process produces a wide range of C_1 to C_{50} products comprising gases, liquid hydrocarbons, oxygenates and water.

Common to each of the above processes is the overriding influence of the capital cost of producing synthesis gas (syngas, H_2+CO). This varies with gasifier design which is in turn influenced by
10 coal properties and product enthalpy. A recent review of gasifier technology has identified some high efficiency gasifiers which of necessity produce relatively low ratios of syngas (H_2+CO) utilizing low ratios of steam and oxygen in the gasification. Thus the most recent advanced gasifiers operate at temperatures requiring relatively low product recovery temperatures and low steam-to-carbon ratios which translate into high thermal efficiency. The syngas produced under these conditions may have a
15 hydrogen/carbon monoxide ratio equal to 1 and more usually for the highest efficiency gasifiers the ratio is less than 1 and within the range of about 0.4 to about 0.7. Such low ratio syngas cannot be directly utilized by present date conventional F—T processes and methanol syntheses, both of which require H_2/CO ratios equal to or greater than 2. Thus any external water-gas shift operation to increase a low ratio syngas of 1 or less up to 2 or more would substantially cancel any gains in efficiency
20 achieved by the most advanced high efficiency gasifiers.

A principal advantage in producing dimethyl ether (DME) directly from syngas is that this compound can be readily converted into gasoline range hydrocarbons using crystalline zeolites represented by ZSM—5, i.e. those having a constraint index of from 1 to 12, for example as discussed in U.S. Patent 3,928,483, wherein formed methanol is dehydrated and the ether product is converted
25 over ZSM—5 crystalline zeolite.

A problem encountered with the synthesis of methanol from syngas is the rather low equilibrium conversion (carbon efficiency) achieved. To attain satisfactory yields in conventional methanol syntheses, it is necessary to recycle large amounts of unreacted hydrogen and carbon monoxide. This factor significantly affects the economic attractiveness of the method, since the large recycle
30 requirement significantly increases the size of the equipment and therefore the capital investment.

Accordingly, improvements have been sought to increase the per-pass methanol productivity or syngas conversion. One approach has been to displace the chemical equilibrium by further reacting methanol to a non-equilibrium end product. Among the displacement reactions suggested has been the dehydration of an intermediate methanol product to form dimethyl ether.
35 For example, U.S. Patent 3,894,102 teaches a two stage process for the conversion of synthesis gas to gasoline wherein synthesis gas is contacted with a mixed methanol-synthesis and acidic-dehydration catalyst to produce a first stage product comprising dimethyl ether and then contacting the intermediate product with a ZSM—5 type catalyst in a second stage to produce aromatic hydrocarbons. Any methanol synthesis catalyst may be employed in the first stage catalyst although a
40 preferred composition is a mixture of Zn/Cu/Cr/rare earth oxides present in the following relative amounts (weights of metals): 50—70 parts Cu, 50—25 parts Zn, and 5—15 parts each of Cr and rare earth. The Cr/(Cu+Zn) ratios of such compositions range from 0.07—0.3.

The syngas employed in the method of U.S. Patent 3,894,102 had a relatively high H_2/CO mole ratio. An important further improvement attainable with the dimethyl ether displacement reaction in
45 the context of syngas conversion over methanol synthesis catalysts is taught by U.S. Patent 4,011,275 which discloses the conversion of syngas having a H_2/CO mole ratio of 0.8 to 1.7 over the two-component dimethyl ether synthesis catalyst. Not only are syngas conversions higher for dimethyl ether/methanol synthesis than for methanol synthesis alone, but maximum equilibrium conversions for the dimethyl ether/methanol synthesis are obtained at feed gas H_2/CO ratios of 1 as compared to 2 for
50 the methanol synthesis. Figures 6 and 8 of the latter patent further show that water addition with the syngas feed shifts the H_2/CO ratio required for maximum equilibrium conversions towards even more hydrogen deficient syngas feeds. Adding carbon dioxide to the feed had no apparent effect on the dimethyl ether/methanol synthesis. Enhanced conversions of the hydrogen/deficient feeds obtained with co-fed water were attributed to the internal water gas shift reaction between the added H_2O and
55 some of the excess CO to produce more hydrogen which is converted to organic product. Methanol synthesis catalyst said to be useful in the latter process include any conventional catalyst.

U.S. Patent 3,098,809 further teaches that dimethyl ether may be produced from a hydrogen-deficient feed mixture containing CO, CO_2 and H_2 by contact under conversion conditions over Cu/Zn/Cr methanol synthesis catalysts and alumina providing that the CO_2 content is low relative to the CO
60 content of the feed gas. The patent teaches that the presence of water in the reacted gas is undesired because it inhibits methanol dehydration, thereby limiting the per-pass conversion to dimethyl ether. Nevertheless, steam addition is said to be useful when CO is in "substantial excess" relative to hydrogen. Suitable methanol synthesis components for the process disclosed are said to include copper-based catalysts and zinc- and chrome-based catalysts. A Cu/Zn/Cr methanol synthesis

component having an atomic ratio of 82/16/4 was employed in the examples. The Cr/(Cu+Zn) ratio of
this catalyst is 0.04. No methods of catalyst preparation are disclosed.

U.S. Patent 4,096,163 suggests the conversion of syngas to hydrocarbon products over a
catalyst comprising a methanol synthesis component and a ZSM—5 type zeolite component. No
5   particular methanol synthesis catalyst is described as being especially desirable.   5

In addition, Sherwin and Blum have reported in an Interim Report for May 1978 under the title
"Liquid Phase Methanol" prepared for Electric Power Research Institute, Palo Alto, California, the
attempt to produce DME by adding gamma-alumina and 13X molecular sieve to a slurry reactor system
containing a commercial methanol synthesis catalyst. At 230—300°C, 35—69 atm. abs. 2015—
10   6915 GHSV (gas hourly space velocity), only traces of DME were observed. A catalyst comprising   10
$Cu/Zn/Cr$ in an atomic ratio of 6/3/1 impregnated on Davidson 980 SiO_2/Al_2O_3 produced trace
amounts of DME at 230°C, 69 atm. a. and 2000 GHSV from a feed containing 50% H_2, 25% CO, 10%
CO_2 and 15% CH_4.

U.S. Patent 4,177,167 teaches that dimethyl ether synthesis catalyst which have been stabilized
15   with silicon compounds exhibit high activity and have longer catalyst service lives relative to   15
unstabilized catalysts. The catalysts are composed of mixtures of oxides or salts of Cr, La, Mn, Cu, Zn
and combinations of the oxides or salts with Al. Atomic contents of Al in the range of 10% to 70% are
required to maintain the activity of the stabilized catalyst. The catalyst may be prepared by any
conventional procedure. Coprecipitation of $Cu/Zn/Cr$ components is exemplified in the specification.
20   The composition of the catalyst (other than the Al content) is not disclosed to have any particular   20
effect. The Cr/(Cu+Zn) ratios of the exemplified catalysts range from about 0.2—0.6. Suitable H_2/CO
molar ratios in the feed gas are disclosed to be within the range of about 0.3 to 10. Syngas employed
in the examples had a H_2/CO ratio of 3.

The feasibility of the direct synthesis of DME was initially demonstrated by a physical mixture of
25   $Cu/Zn/Cr$ containing a rare earth promoter and gamma-alumina. Synthesis gas with an H_2/CO ratio of   25
4 contacted the catalyst at 315°C, 50 atm. a. 1440 GHSV and the conversion obtained was 31.5%
(86% of equilibrium). The product contained 22.4% DME, 0.93% CH_3OH, 29.0% CO_2, 2.0% H_2O, 3.2%
light hydrocarbons and a balance of H_2 and CO. The above catalyst was also tested with $H_2/CO=1$ at
315°C, 103 atm. a. and 4400 GHSV. The conversion dropped from 60% (75% of equilibrium) to 40%
30   in 30 days, indicating rapid aging of the catalyst. Attempted reactivation with H_2 at 315—400°C   30
failed.

Catalyst aging is a significant problem in known dimethyl ether syntheses, since aging severely
limits the commercial practicability of what is otherwise a highly valuable process. The present
invention seeks to provide a reliable and commercially viable process for the regeneration of aged
35   catalysts which have become deactivated by use in dimethyl ether synthesis, thereby rendering the   35
whole process more economically attractive.

The present invention is based on the observations that catalyst aging is minimized by employing
a particular $Zn/Cu/Cr$ catalyst as the methanol synthesis component of the dimethyl ether synthesis
catalyst, and that catalyst activity can be maintained at a high level sufficient to sustain near
40   equilibrium conversion of synthesis gas feed by employing particular oxidative regeneration   40
techniques.

Although the art has recognized the use of such catalysts in dimethyl ether synthesis, the
relationship between catalyst composition, especially its Cr content, and catalyst aging has not
apparently previously been appreciated.
45   Accordingly, the present invention provides a process for converting synthesis gas into dimethyl   45
ether which comprises contacting synthesis gas at a temperature of from 232 to 399°C with a catalyst
composition of coprecipitated Cr, Cu and Zn components and of an acidic dehydrating component, in
which the atomic ratio Cr/(Cu+Zn) is from 0.1 to 1, and subsequently regenerating the catalyst
composition by contacting it with an oxygen-containing gas at from 38 to 538°C.
50   The syngas conversion of the present invention uses the metal components of a methanol   50
synthesis catalyst in combination with an acidic dehydrating component. The catalyst compositions
used in the process of the present invention rely particularly upon the technique of coprecipitation of
the hydrogenating components either alone or mixed with the dehydrating component, the atomic
ratios of Cu, Zn and Cr being variable within the relatively narrow limits specified above. More
55   particularly, coprecipitated components of Cu, Zn and Cr are used in such relative amounts that the   55
ratio Cr/(Cu+Zn) is from 0.1 to 1.0 and more preferably from 0.25 to 0.75. A ratio of 0.5 is particularly
preferred. On the other hand, the ratio of Cu/Zn is preferably from 0.5 to 3.0.

The acidic dehydrating component or matrix supporting material of the catalyst compositions
may be gamma-alumina, silica-alumina, a ZSM—5 crystalline zeolite of high SiO_2 content, a
60   phosphate, titanium oxide in combination with silicon oxide, a rare earth or a clay. Of these materials,   60
gamma-alumina is particularly preferred, especially in an amount comprising about 50% of the catalyst
composition.

The dimethyl ether synthesis techniques of this invention are of special interest since the ratio
H_2/CO may be less than 1 or greater than 1. Thus the ratio H_2/CO may be from 0.5 to 3, more
65   preferably from 0.5 to 2. However, it is particularly preferred to employ gas ratios equal to or less than   65

1, since such gas ratios are much more economically produced by modern high efficiency gasifiers as discussed above, and such a source of syngas can result in from 30 to 40 overall percent reduction in processing costs. In this low ratio (<1) syngas environment, it has been determined that the hydrogen deficiency of low ratio syngas having ratios H_2/CO from 0.4 to 0.7 can be remedied or compensated by
5 injecting steam (H_2O) into the catalyst separately or in admixture with the low ratio syngas charged.   5
This added steam is subject to a water-gas shift reaction by the particular catalyst composition employed, resulting in a very effective and increased H_2/CO ratio gas in the catalyst reaction zone. This particular operation thus eliminates the need for external water-gas shift requirements to modify the low ratio syngas, thereby further contributing to the overall economic improvement of the process.
10   The investigations carried out in developing the present process of converting syngas into   10
dimethyl ether and the concepts developed therefrom have illustrated that certain selected catalyst compositions consisting of coprecipitated mixed oxides of Cu, Zn and Cr mixed with a suitable acid matrix such as gamma-alumina, provide high catalyst activity and selectivity for effecting dimethyl ether synthesis. More importantly, however, was the finding that these catalyst compositions could be
15 periodically oxidatively regenerated to maintain the desired high catalyst activity, that is, the particular   15
catalyst composition used in the present invention can be maintained at high steady-state activity for an extended operating period by relying upon particular oxidative regeneration and pretreatment techniques of relatively short duration. For example, the catalyst in the syngas reaction zone may be regenerated therein or it may be passed through a separate catalyst regeneration zone and then
20 returned to the reaction zone to maintain desired catalyst activity and selectivity. The regeneration of   20
the catalyst therefore may be accomplished in a continuous, semi-continuous or an interrupted, for example periodic, manner depending on whether a fixed bed or a moving catalyst system is employed.
It has been found, for example, that the coprecipitated Cr, Cu, Zn catalyst components admixed with gamma-alumina can be maintained in a high state of activity for achieving substantially
25 thermodynamic yields of DME by periodic regeneration of the catalyst with an oxygen-containing gas   25
of oxygen partial pressure equal to or less than air with a relatively short contact time or until there is a breakthrough of the charged oxygen rich gas. There is no evidence that this has previously been achieved. When using a coprecipitated catalyst as herein defined, it has been found that the catalyst can be successfully regenerated at a temperature of 38 to 538°C, it being preferred to employ
30 temperatures below 538°C for any extended operating period. Following oxidation or regeneration of   30
the catalyst, it is important, if not essential, to avoid contacting the freshly oxidized catalyst with a high-temperature reducing gas. That is, reducing the freshly regenerated catalyst with hydrogen, a hydrogen-carbon monoxide mixture or any other reducing gas should be avoided, particularly where the contact temperature is equal to or above 260°C. It is preferred, therefore, to contact the oxygen-   35
35 regenerated catalyst with a reducing gas such as a syngas feed or a diluted syngas initially at a
temperature of 177°C to about 232°C and thereafter raise the temperature and/or change the composition of the syngas feed to achieve near thermodynamic yields of DME.
Regeneration of the catalyst may be accomplished periodically or continuously, depending on whether a fixed or moving catalyst system is employed. Furthermore, conversion of the low ratio   40
40 syngas into DME may be effected under gradually decreasing conversion conditions below equilibrium
conditions, in which case the catalyst may be retained in on-stream use for a greater length of time before requiring oxidative regeneration. Thus the oxidative regeneration of the catalyst is critical to the extent that very high temperature exotherms are to be avoided about catalyst particles being oxidatively contacted. Frequent regeneration of catalyst used in a swing reactor system permitting   45
45 weekly or even daily regeneration or regeneration at an intermediate frequency may be used to
advantage. Daily regeneration of the catalyst mass is desirable when converting the syngas to achieve substantially equilibrium yields of DME and the regeneration temperature should preferably be kept below about 538°C to maintain more optimum catalyst activity.
The present invention is described and illustrated in more detail below with reference to the   50
50 accompanying drawings, in which
Figures 1 to 4 illustrate the various aspects of co-feeding water with syngas to the catalyst;
Figure 5 is a block flow diagram of the conversion of syngas into liquid fuels;
Figure 6 illustrates the effect of catalyst composition on catalyst decay;
Figure 7 illustrates the effect of catalyst preparation on catalyst performance;   55
55 Figures 8 and 9 illustrate aspects of catalyst regeneration; and
Figures 10 to 14 illustrate aspects of catalyst preparation and composition on catalyst performance.
As mentioned above, dimethyl ether synthesis effects decisive advantages over other F—T and methanol synthesis operations since it lends itself particularly to utilization of relatively low ratio   60
60 syngas, and this particular feature can be used to advantage in combination with any high efficiency
gasifying operation producing low ratio syngas (H_2/CO less than 1) by the injection or addition of steam as required with the low ratio syngas feed. In this operation, the catalyst's water-gas shift capability is utilized to advantage.
Figure 1 of the accompanying drawings is a graphical representation of total H_2 and CO   65
65 conversion against moles of water (steam) fed to the catalyst per 100 moles of syngas and illustrates

one effect of co-fed steam. The H_2/CO ratio was 0.67, the temperature was 316°C and the pressures were 50, 75 and 100 atmospheres. As can be seen from Figure 1, the conversion goes through a maximum which shifts to higher relative amounts of co-fed steam with increased pressure. It is apparent therefore that maximum conversions are somewhat lower than those for $H_2/CO=1$ at
5 comparable total pressures.

The direct synthesis of dimethyl ether from synthesis gas can be utilized with considerable advantage in many different combination operations, that is to say the economic formation of dimethyl ether from low ratio syngas obtained from an efficient syngas generation or obtained by *in situ* gasification of coal, is particularly instrumental in competitive routes for producing specific chemicals
10 and/or hydrocarbons varying considerably in composition.

For example, the co-feeding of water with low ratio syngas has a principal effect of increasing the syngas utilization via the shift reaction with excess CO to form additional hydrogen. An additional but equally unimportant effect of the co-fed water is an increase in the H_2/CO ratio of the recovered effluent of the syngas conversion up to at least a H_2/CO ratio of 1. This effect of upgrading the H_2/CO
15 ratio in the recovered effluent is illustrated in Figure 2 of the accompanying drawings, which is a graphical representation of the H_2/CO ratio of the exit gas from a syngas conversion catalyst zone, against moles of water (steam) fed to the catalyst per 100 moles of syngas. The initial H_2/CO ratio was 0.67, the temperature was 316°C and the pressures were 50, 75 and 100 atmospheres.

The DME product of the synthesis of the present invention may be upgraded to methyl t-butyl
20 ether by reaction with a suitable alcohol, for example, t-butanol or by reaction with a branched olefin, for example, 2-methylpropene utilizing an acid catalyst. The acid catalyst may be sulfuric acid or a mineral acid with or without a support material. Alternatively, the acid catalyst may be an acidic ion exchange resin, or phosphoric acid on a support material. The operating temperature may be from 50°C to 300°C, with a temperature of from 60°C to 150°C being particularly preferred. A pressure of
25 from 3 to 50 atmospheres is suitable for this operation.

In another process, the syngas initially obtained from a gasification operation can be converted into a product rich in dimethyl ether in a catalyst slurry reaction system. In such a system, the metal and acid components of the catalyst are surrounded by or suspended in a suitable high boiling liquid phase, for example a mineral oil, an oil product of a Fischer-Tropsch synthesis such as a portion of the
30 decant oil product, and a lubricating oil base stock. The solid catalyst components may be used as combined particles or as separate particles of the metal and acidic components. This liquid phase operation will generally be carried out a temperature of from about 260°C to about 343°C at a pressure of from about 68 to 136 atmospheres.

In yet another process, the DME product may be converted into methanol by reaction with water
35 in the presence of an acid catalyst. The catalyst may be phosphorus pentoxie (P_2O_5) distributed on kieselguhr, silica-alumina, alumina, reduced tungsten oxide or an acid crystalline zeolite. The temperature will generally be from about 204°C to about 371°C and the pressure will generally be from 10 to 100 atmospheres.

Alternatively, the DME product may be reacted with oxygen in the presence of a copper catalyst
40 to form formaldehyde. In such an operation, the temperature may be from about 600°C to 720°C and the pressure from 1 to 5 atmospheres. Instead of the copper catalyst, there may be used tungsten oxide in combination with phosphoric acid distributed in a carrier material such as alumina, silica-alumina or kieselguhr, or silver alone or promoted with small amounts of copper and silver. When using a silver catalyst, the temperatures will generally be from 600°C to 800°C and the pressure from 3 to 8
45 atmospheres. Still further, there may be used a catalyst mixture comprising iron promoted with molybdenum (for example 18% Fe_2O_3+82% MoO_3 by weight) at a temperature of from 350°C to 400°C.

Still further, liquid fuels may be prepared, relying upon an olefin intermediate product of DME conversion as feed to a liquid fuels conversion operation. That is, the DME product is converted at a
50 temperature of from 343 to 427°C and preferably of at least 371°C into an olefin intermediate product by contact with a crystalline zeolite represented by HZSM—5 crystalline zeolite. The olefins formed may be branched or straight chained olefins, depending upon the conditions employed and the catalyst activity, and suitably boil within the gasoline boiling range. Alternatively, the operating conditions and catalyst may be selected to produce an aromatic-rich gasoline product from the olefins formed. Still
55 further, the olefin intermediates may be upgraded to a jet fuel product by the combination of olefin oligomerization or olefination and hydrogenation. Oligomerization of the olefin intermediate may be accomplished at a temperature of from 175°C to about 250°C, it being particularly preferred to employ a temperature of from 200 to 220°C and a pressure of from 10 to 100 atmospheres. When effecting the oligomerization of olefins to form jet fuel, it is desirable to co-feed water and to maintain
60 about 15 to 18% free P_2O_5 in the catalyst composition. Kieselguhr may be used as the acid catalyst support material.

The synthesis of olefins from the DME product is an intermediate step in a combination of steps leading to the production of chemical constituents, branched olefins, aromatics and gasoline boiling range materials depending on reaction conditions and catalyst employed. In addition to the above-

defined combinations, it is also recognized that a mixture of olefins from any source in addition to those produced from DME may be reacted with methanol to form high-octane ethers.

In yet another alternative, unreacted syngas may be separated from the DME product. This unreacted syngas, normally having a H_2/CO ratio of at least 1, comprises substantial amounts of CO_2.

5 Such a syngas composition can be used to advantage in a Fischer-Tropsch syngas conversion operation utilizing iron or cobalt or ruthenium as the Fischer-Tropsch metal component. Thus, the unreacted syngas of the DME synthesis can be converted in a Fischer-Tropsch synthesis in the presence or absence of a water-gas shift metal component.

In any of the above processes, unreacted syngas may be recycled to the DME conversion 10 operation before or after CO_2 removal as required, and with or without the addition of water to the recycle gas. On the other hand, the total unreacted gas comprising CO_2 may be passed to a Fischer-Tropsch syngas conversion operation with or without co-fed water and reacted to form a broad spectrum of products.

Referring now to Figure 5 of the accompanying drawings, there is shown a block flow diagram of 15 a plant for upgrading syngas, following the processing procedures of the invention. A low ratio syngas having an H_2/CO ratio of 1 or less is charged to the process by conduit 2 for conversion thereof to dimethyl ether in zone 4. Water is charged separately to zone 4 by conduit 6 or passed by conduit 8 and mixed with syngas in conduit 2 before passing to DME synthesis zone 4. In zone 4, the conditions of temperature, pressure and space velocity are selected to produce a product rich in DME but 20 containing some methanol. Zone 4 also encompasses a separation facility wherein unreacted syngas and CO_2 are separated from the DME-rich product. Unreacted syngas and CO_2 are recovered by conduit 10 for further treatment. The DME-rich product comprising methanol and CO_2 is recovered and withdrawn by conduit 12. The DME-rich product is passed by conduit 12 to zone 14 where the ether is converted into gasoline boiling range olefins and/or aromatics by contact with a crystalline zeolite 25 catalyst represented by ZSM—5. Methanol in the recovered DME product is also converted to gasoline boiling range materials by contact with the zeolite catalyst. The reactions contemplated in zone 14 are those of olefination, polymerization and aromatization under operating conditions particularly selective for the purpose with the catalyst employed. The zeolite catalyst component may be provided with some hydrogenation activity by the addition of one or more of cobalt, iron, platinum, palladium, 30 ruthenium, rhodium, osmium, copper, zinc, manganese and molybdenum. An olefinic and/or aromatic gasoline boiling range product is recovered as the product of this operation by conduit 16.

The enriched H_2/CO syngas comprising CO_2 recovered from zone 4 by conduit 10, is passed to zone 18 comprising a Fischer-Tropsch catalyst wherein the enriched syngas in the presence or absence of added water is subjected to a Fischer-Tropsch type of syngas conversion. The reactions 35 contemplated in zone 18 are those of Fischer-Tropsch synthesis provided by iron, cobalt and ruthenium catalysts particularly, although other components such as osmium and rhodium may also be employed with varying success. On the other hand, the Fischer-Tropsch metal component may be in admixture with a zeolite or acidic carrier material modified to adjust the activity of the individual components within a desired range. The Fischer-Tropsch component may also be in admixture with a crystalline 40 zeolite represented by ZSM—5 crystalline zeolite to effect conversion of the syngas into particularly gasoline boiling range components. The catalyst employed in zone 18 may be in a fluid grid or fixed catalyst bed reactor system or suspended in a liquid phase reactor system. In this manner, the syngas may be converted over a Fischer-Tropsch catalyst such as iron modified with potassium to produce a mixture of C_1 to C_{50} carbon components comprising alcohols, oxygenates and hydrocarbons. The 45 Fischer-Tropsch synthesis is normally carried out at a temperature of 149 to 427°C and at a pressure of from 3.5 to 136 atmospheres. The products of the Fischer-Tropsch synthesis are normally separated to recover C_4 and lower-boiling components from gasoline boiling range material and a high-boiling decant oil product. Oxygenates are recovered in a water phase and thereafter converted with ZSM—5 to hydrocarbons.

50 The upgrading of the product of Fischer-Tropsch synthesis may proceed along a number of different routes described in recent publications. It is particularly desired to process the Fischer-Tropsch product in accordance with one or more of these publications to obtain LPG, gasoline and diesel fuel products.

For example, upgrading the unreacted syngas obtained from the DME synthesis may be achieved 55 by the techniques described in U.S. Patents 4,086,262; 4,157,338; and 4,159,995, and/or the total product of the Fischer-Tropsch synthesis may be processed by the techniques described in U.S. Patents 4,041,094; 4,046,830; and 4,046,831. Alternatively, the product of the Fischer-Tropsch synthesis may be separated so that gasoline boiling material and lower boiling material are processed by the techniques of U.S. Patents 4,041,095; 4,045,505; 4,049,741; and 4,052,477. Material higher boiling 60 than gasoline and referred to as the decant oil product may be processed by the techniques of U.S. Patents 4,044,064; 4,046,829; 4,053,532; 4,059,648; and 4,071,574.

In the processing arrangement of Figure 5 and in accordance with a specific method of operation, the syngas comprising CO_2 is processed over a Fischer-Tropsch synthesis catalyst in zone 18 to produce a product effluent comprising alcohols, oxygenates and hydrocarbons. The product effluent is 65 separated in zone 18 to recover hydrocarbons which are passed by conduit 20 to zone 22. In zone 22,

the hydrocarbons are converted over one or more catalyst masses comprising a crystalline zeolite represented by ZSM—5 crystalline zeolite providing a pore opening of at least 5 Angstroms, a silica to alumina ratio greater than 12 and a constraint index within the range of 1 to 12. In this catalyst operation, temperature and pressure conditions are selected to achieve upgrading of the charged
5   hydrocarbons to form LPG, a relatively high octane gasoline, diesel and/or jet fuel of desired freeze and   5
pour point characteristics. The conditions of operation may be varied considerably, depending on the particular hydrocarbon fraction treated and the desire to produce one or more fractions of LPG, gasoline of higher octane rating, diesel and jet fuel products.

The tests described below were carried out in a microreactor with related system components
10   which permitted rapid catalyst loading and pretreatment and ready adjustment of reaction conditions,   10
feed gas mixtures and regeneration conditions without disturbing the catalyst. The reactor was 400 mm in length and made from a 9.525 mm external diameter 304 stainless steel (SS) tube with an annular 3.175 mm external diameter 304 SS thermowell running the entire length of the bed of catalyst therein. A 3.0 cc catalyst bed (90 mm long) was centrally positioned in a 300 mm vertical tube
15   furnace. The catalyst bed was held in place by vycor glass wool supported by pyrex tubes filling the   15
reactor voids. Temperature was maintained by a proportional band controller with a thermocouple located in the furnace wall near the reactor. During use, premixed H_2 and CO was compressed and fed through activated charcoal traps (the charcoal was necessary to remove traces of iron carbonyl present in the feed gas cylinders). Constant gas flow was maintained by a thermal mass flow controller and
20   reactor pressure was maintained by a back-pressure regulator downstream of the reactor and liquid   20
traps.

I catalyst preparation and pretreatment

Catalysts I to VI were prepared by coprecipitation of the desired metals from hot (85—90°C) aqueous solutions of the nitrates by the slow addition of hot aqueous sodium carbonate (>100%
25   excess carbonate).   25
The precipitate was filtered and washed until free of carbonate in the wash. The washed precipitate was dried in a vacuum oven (70°C) and calcined in air for at least 6 hours. Spot analyses of the calcined powders for copper, zinc, chrome and sodium indicated that the metals were present in the final material in the same ratios as in the initial nitrate solutions and that sodium had been
30   essentially removed. Details of these preparations are set out in Table 1 below.   30
The calcined powders (—80 mesh) were then each physically mixed with an equal weight of powdered gamma-alumina as acidic dehydration component (which had been calcined at 538°C for at least 6 hours) and the mixture was machine pelleted and crushed to 10/30 mesh.

Each of the resulting catalyst compositions was then pretreated in the reactor at 204°C in a
35   reducing H_2/N_2 stream (1 atmosphere, GHSV 1500) whose hydrogen partial pressure was slowly   35
increased by raising the hydrogen content from 0 to 2 volume % and then to 8.5 volume %. The pretreated catalyst was then cooled to below 49°C in an inert gas stream, the reactor feed switched to syngas at the pressure and space velocity desired and the temperature increased.

A further catalyst (Catalyst VII) was prepared as follows: a portion of the carbonate-preprecipitated
40   methanol component used for the Example II catalyst was calcined at 260°C; a portion of the resulting   40
powder was combined with an equal weight of gamma-alumina, pelleted and crushed, and a 10/30 mesh portion selected with an apparent density of 1.05 gm/ml. The Cr/(Cu+Zn) ratio for this catalyst was 0.5.

A 3 ml portion of Catalyst VII was loaded into the tubular reactor and was pretreated and put on
45   stream in the manner described above.   45
An additional catalyst (Catalyst VIII) was also prepared, as follows: a solution was prepared by dissolving the amounts of Cu-, Zn- and Cr-nitrates indicated for Catalyst VI in Table 1 in 170 ml of water; a precipitate was obtained when 41.5 ml of NH_4OH (29%) solution was slowly added, the pH reaching 7.5; this precipitate was washed three times with 1 to 1.5 liters of water, dried in a vacuum
50   oven (140°C) and calcined at 357°C; a portion of the resulting powder was combined with an equal   50
weight of gamma-alumina, pelleted and crushed, and a 10/30 mesh portion selected. The resulting DME catalyst differed principally from that of Catalyst VI in that the metals in the methanol catalyst component were precipitated by ammonia rather than carbonate.

Table 1
Metal components of dimethyl ether synthesis
Catalyst preparation details

Example catalyst	I	II	III	IV	V	VI
5 Solution A water (ml)	500	200	200	300	200	200	5
Cr $(NO_3)_3 \cdot 9H_2O$ (gm)	52.7	48.03	74.1	136.3	74.1	92.6
Cu $(NO_3)_2 \cdot 3H_2O$ (gm)	220.1	29.	22.4	22.4	34.4	22.9
Zn $(NO_3)_2 \cdot 6H_2O$ (gm)	130.5	35.71	27.5	27.5	13.9	9.2
La $(NO_3)_2 \cdot 6H_2O$ (gm)	71.6*	—	—	—	—	—
10 Solution B water (ml)	2500	550	300	300	550	550	10
Na$_2$CO$_3$ (gm)	400	111.3	54	81.2	100.0	100
Temp. of Precipitation (°C)	90	85—90	90	85—90	90	95
pH of Filtrate	—	9.8	8.0	8.16	9.95	9.4
Temp of Calcination (°C)	265	338	274	267	338	260
15 Cr/(Cu+Zn)	0.14	0.50	1.0	1.8	1.0	1.8	15
Cu/Zn	2.06	1.0	1.0	1.0	3.0	3.1

DME synthesis catalyst prepared by combining the above powders with an equal weight of calcined gamma-alumina.

*Analysis of final metal composition indicated 3 atom percent lanthanum based on the methanol catalyst components.

As will be seen from Table 1, the compositions of the catalyst varied. This enabled comparisons to be made of the effects of chrome composition at three similar Cu/Zn ratios and the effect of Cu/Zn composition at similar chrome levels.

II Catalyst aging characteristics

The aging characteristics of each catalyst were quantified by the slope associated with a plot of $1n(—1n(1—Q))$ versus days on stream, where Q is the ratio of the observed total syngas conversion to that predicted for thermodynamic equilibrium. The negative of this slope is the decay rate for an exponential deactivation expression. This concept results when the decay rate expression

$$K=K_o e^{-bt} \tag{1}$$

where K is an empirical reaction rate term; K_o is the value of this term for fresh catalyst, b is the decay parameter and t is the time on stream, is substituted into an empirical reactor model

$$1n(1—X/Xeq)= —K/GHSV \tag{2}$$

where X is the observed total molar conversion of H$_2$+CO, Xeq is the equilibrium value, and GHSV is the gas hourly space velocity for the reaction. Substituting equation (1) into equation (2) and linearizing gives the expression

$$1n(—1n(1—X/Xeq))=1n(K_o/GHSV)—bt \tag{3}$$

In Table 2 below, details of the experimental conditions for each of the six catalysts described in Table 1 are presented along with the values of the decay constant (b) obtained by a least-squares fit of the reaction expression of equation (3). In Figure 6 of the accompanying drawings, the value of the decay constant is plotted against the chrome composition of each of the six catalysts as expressed by the ratio Cr/(Cu+Zn).

Table 2
Effect of catalyst composition on catalyst aging

Example catalyst	I	II	III	IV	V	VI	
Reaction Conditions with a Feed							5
5 H_2/CO Ratio of 1/1:							
Pressure Atm.	100	100	100	100	100	100	
Temperature (°C)	316	317	315	314	316	316	
GHSV	3800	4000	4000	4000	4000	4000	
Days of Aging	40	48	38	20	24	42	
10 Catalyst Composition:							10
Cr/(Cu+Zn)	0.14	0.50	1.0	1.0	1.8	1.8	
Cu/Zn	2.1	1.0	1.0	3.0	1.0	3.1	
Decay Parameter Value (least-squares correlation)							
15 b, days^{-1}	.040	.013	.030	.029	.032	.027	15

From these tests, it is apparent that catalyst performance is best for compositions of Cr/(Cu+Zn) ratio from about 0.1 to about 1.0, with a preferred Cr/(Cu+Zn) ratio of about 0.5. Deviations from this behavior occur for low Cu/Zn (0.5) and for a commerically available methanol catalyst prepared other than by coprecipitation. It was also determined from a study of catalyst aging data of catalyst
20 comprising 25, 50 and 83% Al_2O_3, that the aging behavior of catalysts with 50% alumina is preferable.   20
For a high-chrome-containing catalyst, the effect of ammonia or carbonate precipitation on activity was contrasted. A lower conversion activity was found for the catalyst prepared by ammonia precipitation (see below and Figure 7 of the accompanying drawings). Carbonate precipitation was thereafter adopted for catalyst preparation.

25   III Catalyst regeneration   25
It was recognized at an early stage in the development of the invention that above about 288°C, the aging of a DME synthesis catalyst is associated mainly with aging of the methanol catalyst components. The detailed aging mechanism of methanol synthesis catalysts is not known but causes for aging can be assumed to be (1) coke deposition, (2) catalyst phase changes, and (3) changes in
30 oxidation state. A fourth possibility is the strong competitive sorption of CO, especially when H_2-lean   30
feeds are used.
Some exploratory studies on copper-based DME synthesis catalysts provided the following observations: (1) a spent catalyst, aged for 20 days, which had lost 30% of its activity, analyzed 1.3% coke (0.001% of feed); (2) calcination of this catalyst in air at 538°C for 16 hours led to further
35 deactivation; (3) samples of spent catalyst showed no CO chemisorption capacity; and (4) treatment of   35
the spent or aged catalyst with H_2 was not effective in restoring activity. The state in which the components of the active catalyst exist is not known, but there is evidence to suggest that when copper is reduced to its metallic state, the catalyst is no longer active and a catalyst which has been subjected to too severe oxidation treatment is also not active. Also, it has been suggested that the
40 active catalyst is one in which copper exists in the Cu^I state (see, for example, Journal of Catalysis 56,   40
407—429 (1979) in which a solution of Cu^I in ZnO was reported to be the active component in
Cu/ZnO, Cu/ZnO/Al_2O_3 and Cu/ZnO/Cr_2O_3 low-pressure methanol synthesis catalysts). Further, the quantitative absorption of CO by Cu^I solutions is known, as taught by F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry", 2nd Ed., Interscience Publ., London, 1968, page 898. Thus it can be
45 speculated that the loss of CO chemisorption capacity of the catalyst and thus catalyst activity can be   45
associated with reduction of the Cu^I state.
In an effort to maintain the activity of the DME-producing catalysts used in this invention over an extended period of operation, the following tests were carried out.
Oxidation treatments of the Cr/Cu/Zn/γ-Al_2O_3 catalyst compositions were carried out by
50 connecting a vessel containing pure or dilute oxygen in an inert gas (helium) to the reactor inlet. Inert   50
purge gas was then charged to the vessel, diffusively mixing with and carrying its contents to the aged catalyst. After oxygen treatment, the vessel and the reactor containing the catalyst were brought to reaction pressure and temperature with helium. The feed stream inlet was then switched to syngas. Diffusional mixing in the vessel upstream of the reactor resulted in a gradual shift to primarily syngas
55 concomitantly with a temperature adjusted reaction. With this system, the frequency, duration, partial   55
pressure and amount of oxygen used during regeneration were varied. Oxidation studies conducted in this manner established a regeneration operation which reactivated and substantially stabilized the dimethyl ether synthesis catalysts.
Initial studies were conducted on a Cu:Zn:Cr=1:1:1+50% gamma-alumina catalyst aged for 105
60 days to 20% conversion (the catalyst of Example II).   60
The minimum effective oxygen partial pressure for treatment at reactor conditions (100 atm.

GHSV 4000) with a 100 liter/liter-catalyst pulse was determined. Treatments at four oxygen partial pressures (0.1, 1, 4 and 2 atm.) were performed at high (100 atm.) total pressures and a temperature in the range of 307 to 338°C. The results obtained are summarized in the first four examples of Table 3 below. After regeneration, initial conversions were enhanced by as much as 140%. However, the
5   regenerated catalysts subsequently aged, with projected conversions relaxing to preregeneration levels   5
after about 10 days. It is therefore apparent that oxygen partial pressures greater than 0.1 atm. and of about 1 to 4 atm. or higher are preferred for treatment at high total pressure and 100 liter-gas/liter-catalyst pulse volumes.
     The total volumes of oxygen contacting the catalyst during regeneration were then increased as
10   provided in the last three examples of Table 3. In these regenerations, the oxygen partial pressure was   10
retained at about 1 atmosphere; however, the temperature of the oxidation treatment was increased. It will be observed from Table 3 that the catalyst activity dropped as evidenced by changes in conversion following oxygen treatment of the catalyst. For example, after 108.8 days of operation the catalyst was oxygen regenerated and its activity restored to a conversion level of 47.6. The activity then declined to
15   a conversion level of 37.4 and after 114.0 days of operations its activity was restored by oxidation to a   15
conversion level of 47.1. After being treated with large volumes of oxygen as provided in the last three examples, the catalyst activity was restored to conversion levels of 55.8, 56.6 and 44.8.

Table 3

Material balances before and 16 hours after indicated oxygen treatment

Oxygen treatment							
Volume O_2 l (STP)/l-cat.	10.0	100	400	200	2100	5000	500
Partial Pressure O_2 atm.	.1	1	4	2	1	1	1
Total pressure (He Dilute) atm.	100	100	100	100	100	1	1
GHSV of O_2	4000	4000	4000	4000	100	900	900
Temperature (°C)	307	338	309	321	293	458	514

Reaction Conditions:														
DAYS OPR	104.0	104.8	105.8	108.8	112.8	114.0	119.0	120.0	122.0	123.0	125.0	126.0	127.0	128.0
T RXR °C	315	315	317	317	316	318	317	371	316	317	316	315	316	315
P atm.	100.03	99.35	99.35	99.35	99.35	99.35	99.35	99.35	99.35	99.35	99.35	99.35	99.35	99.35
GHSV	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000
WHSV	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18	3.18
KG/L/HR	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68	2.68
Conversion [Mole%]:														
H_2	20.8	25.8	26.6	49.2	35.9	51.1	31.4	46.8	32.6	60.8	48.0	59.6	44.4	47.3
CO	18.2	20.8	19.6	46.0	38.9	43.1	23.5	38.6	24.7	50.8	43.2	53.5	42.0	42.2
TOTAL	19.5	23.3	23.1	47.6	37.4	47.1	27.5	42.7	28.6	55.8	45.6	56.6	43.2	44.8

A second regeneration study for a Cu:Zn:Cr=1:1:1+25% alumina catalyst which had been aged for 50 days to 29% conversion was pursued. During eleven cycles of oxidative pulses (1 atm. O_2 at 100 atm. and 100 liter/liter-catalyst every fifth day), conversions were maintained above 45%. Between 95 and 101 days and 104 and 108 days, similar daily oxidative treatments maintained a mean minimum
5   conversion level of 44% (±2.6%). Between 101 and 104 days, the oxidative pulse volume was reduced   5
to 25 liter/liter-catalyst. During this 3-day period, conversion dropped from 42% to 36%, clearly indicating that the more severe (100 liter/liter-catalyst at 1 atm. O_2) oxygen treatment is preferred.

After 68 days in this experiment, the oxidative pulse was followed by the hydrogen treatment procedure used to "activate" or pretreat fresh catalyst. The catalyst performance following this treat-
10   ment indicated little, if any, regeneration improvement. The hydrogen treatment used was apparently   10
sufficient to deactivate those sites regenerated by the oxidative step.

During the last two cycles (107 and 108 days), the oxidative treatment was conducted at a total pressure of 1 atmosphere with pure oxygen instead of 100 atm. at 1% oxygen. No major differences in regenerated catalyst conversion activity were observed. So long as the initial partial pressure of oxygen
15   in the pulse was maintained at about 1 atmosphere, it appeared that inert gases could be used to   15
maintain any practical total pressure (1—100 atm).

In a third study, fresh catalyst (Cu:Zn:Cr=1:1:1+50% alumina) was initially subjected to 3-day and daily regeneration cycles (1 atm. O_2; 100 atm. total; 100 liters-O_2/liter-catalyst; 293—343°C; GHSV (O_2)=70—600) for reaction conditions at high space velocity (GHSV=4000; 316°C; 100 atm.;
20   H_2/CO=1). Then a daily regeneration schedule following a no-regeneration period was conducted for   20
reaction conditions at low space velocity (GHSV=2000; 316°C; 100 atm.; H_2/CO=1) with a long period (24 cycles) of daily regeneration (1 atm. total; 1 atm. O_2; 100 liters-O_2/liter-catalyst; 293—343°C; GHSV (O_2)=70—600). This shows that stable operation at essentially equilibrium conversion can be maintained by daily regeneration. The results of this test are set out in Figure 8 of the
25   accompanying drawings.   25
In a further test, catalyst VII was operated for 50 days on stream with periodic oxidative regenerations. The nominal reaction conditions were 100 atm. pressure, a temperature of 316°C, a feed of synthesis gas with a ratio of H_2/CO of 1/1 (molar) and a GHSV of 4300 for the first 28 days on stream, 3000 for the 29th day, and 2000 for 30 to 49.5 days on stream. Periodic oxidative
30   regeneration of this catalyst was accomplished in the following two operating modes: 30

A. For the first 28 days on stream, the oxidative regeneration procedure was:
1. Flush the reactor with helium at 100 atm. pressure.
2. Elute a 1% oxygen-in-helium mixture at a pressure of 100 atm. from a container of volume 100 (l/l) liter/liter catalyst (i.e. 100 l—O_2 at STP/l catalyst) at GHSV of 7000 (catalyst
35   temperatures were maintained between 271°C and about 316°C during this step).   35
3. Flush with helium at 1·00 atm.
4. Bring synthesis gas into the reactor to resume reaction at 316°C and 100 atm. by passing a 100% syngas stream to the reactor through a "buffer" container of helium 100 l/l catalyst at a GHSV 4300.

40   B. During oxidative regeneration after 28 days: 40
1. Depressurize the reactor to atmospheric pressure and flush in helium.
2. Elute a pulse of 100% oxygen from a container of volume 100 liter/liter catalyst (i.e. 100 liters O_2 at STP/liter catalyst) at 1 atmosphere pressure with helium at a GHSV of about 600 and temperatures of between about 260°C and 316°C.
45   3. Flush and pressurize the system to 1460 atm. with helium.   45
4. Resume 100% syngas charge to the reactor as per step 4 operating mode A above and then drop the GHSV to the desired value of 2000 (or 3000).

It was found that while 3-day cycles were not effective in maintaining stable operation at 4000 GHSV, a week of stable operation at 56% conversion (70% of equilibrium) was maintained with daily,
50   low severity regeneration cycles. Statistical correlation of this data indicated essentially "steady state"   50
activity.
At the lower feed rate (GHSV=2000), catalyst aging was present without regeneration. However, daily regeneration allowed the maintenance of essentially equilibrium conversion (79% vs. 80%) for 20 days of operation (24 cycles). Material balances were performed at the end of each cycle. Aging was
55   not statistically significant.   55
A major conclusion of this catalyst study is that above 50% equilibrium conversion levels and up to substantially 80% conversion levels can be maintained with stable catalyst behavior for dimethyl ether synthesis. However, periodic or a relatively continuous, low severity oxidative regeneration of the catalyst is desirable to maintain this conversion level.
60   In a final test, Catalyst VIII (ammonia precipitated) was operated for several days at the nominal   60
reaction conditions of 100 atm. pressure, a temperature of 316°C, a synthesis gas with a feed ratio of

H_2/CO of I/I (molar) and a GHSV of 4000. The performance of Catalyst VIII is compared with that of Catalyst VI in Figure 7 of the accompanying drawings.

IV Effect of catalyst preparation on regeneration

To further establish the criticality of the presence of Cr in the methanol synthesis component of the dimethyl ether catalyst of this invention and of the effect of the coprecipitation preparation technique, the responses of various catalyst preparations to mild oxidative regeneration were studied. Details of the catalyst modifications investigated are set out in Table 4. The dimethyl ether synthesis catalysts were pelleted from physical mixtures of equal parts by weight of γ-alumina and a methanol component. Catalysts IX and X were prepared by the coprecipitations of the Cr/Zn/Cr or Cu/Zn/Al combinations with excess Na_2CO_3 solution (final pH 9) from solutions of the nitrate salts, followed by calcination at 260°C. Catalyst XI was prepared by carbonate coprecipitation of the Cu/Zn pair followed by calcination at 343°C. Catalyst XII was prepared by carbonate precipitation of the Cu/Zn pair, calcination at 343°C, and high-shear slurry mixing with Al in a water suspension in a Wang blender according to the procedure described in U.S. Patent 3,790,505. Catalyst XIII was prepared by carbonate precipitation of the Cu/Cr and Zn/Cr pairs and subsequent mixture of their calcined (260°C) powders. Further details of these catalyst preparations are similar to those described above, for example all catalysts were activated with dilute, low temperature hydrogen in a manner designed to avoid undesired exotherms.

Syngas conversion studies were conducted on these catalysts in the apparatus described above (316°C, 100 atmospheres, H_2/CO=1 and GHSV=4000, except for Catalyst IX where GHSV=4000 to day 28 and then GHSV=2000). Periodic oxidative regeneration were performed according to the operation mode "B", described above, except that the temperatures were from 288 to 343°C.

The regeneration behavior of the Cu/Zn/Cr base case is illustrated in Figure 10. As with the data illustrated in Figure 8, this data shows the renewed activity resulting from oxidative regeneration of Catalyst IX. Constant conversion can be maintained with sufficiently frequent periodic regeneration.

The effects of coprecipitating the modifiers Cr and Al can be compared in Figures 10 and 11 with the situation where the modifier is absent in Figure 12. Initial conversion activities are quite similar. However, when modifiers are absent even initial regeneration of Catalyst XI was fruitless. Thus, it is essential that the Cu/Zn components be stabilized with structural promoters.

Table 4
Dimethyl ether synthesis catalysts-methanol components

Catalyst	Methanol component composition and preparation	Note
IX	Cu/Zn/Cr=1/1/1, carbonate-precipitated	Base Case
XI	Cu/Zn/Al=1/1/1, carbonate-precipitated	Substitute Al for Cr "Stabilizer"
XII	Cu/Zn=1/1, carbonate-precipitated	Eliminate Al or Cr "Stabilizer"
X	Cu/Zn/Al=1/1/1.5 Cu&Zn carbonate-precipitated, Al_2O_3 high-shear mixed	High-shear mixed alumina addition
XIII	Cu/Cr+Zn/Cr=1/0.5+1/0.5	Effect of separate coprecipitation of active metals with Cr

Incorporation of an Al modifier by physical mixing is illustrated in Figure 13. Activity and aging of this catalyst (Catalyst XII) closely parallel those of the unmodified Catalyst XI (Figure 12). The aged catalyst could not be regenerated. Clearly, the modifier must be coprecipitated with the active metals.

The case for which half of the modifying chromium was coprecipitated with copper and the other half coprecipitated with zinc and the resultant calcined powders combined with the dehydration component to form a DME catalyst (Catalyst XIII) supports this conclusion. While less active, this catalyst was regenerable as illustrated in Figure 14. The greatly reduced activity of this combination is consistent with the hypothesis that the active methanol synthesis site involves copper in solid solution with the zinc oxide phase of the methanol component.

Coprecipitated Cu/Zn/Al-based DME catalysts appear to be initially characterized by a higher recovery activity (activity after regeneration) than the Cr modified counterpart (Figure 11 vs. Figure 10). However, after a 40 day period and 4 oxidative treatments, the Al modified catalyst was no longer regenerable.

Clearly, the coprecipitated Cu/Zn/Cr-based DME catalyst of this invention exhibit remarkable stability to regeneration. Steady high conversion has been observed at GHSV=2000 for 80 days and over 45 cycles. Even at GHSV=4000, the catalyst was oxidatively regenerable after 125 days and 5 cycles.

13

Figure 9 illustrates data collected to identify the severity (temperature) limits for oxidative regeneration. Conversion was carried out at 316°C, 100 atmospheres and GHSV 4000 using a syngas of $H_2/CO=1$ over a Cu/Zn/Cr (l/l/l)-based catalyst. Regeneration conditions were as follows:

Run	Temperature, °C	Pressure, atm.	O_2, mole%
a*	316	100	0.1
b	316	100	1
c	316	100	4
d	316	100	2
e**	293	1	100
f	399	1	100
g	454	1	100
h	510	1	100***
i	316	1	100
j	293	1	100

5

10

*catalyst ages for 104 days to below 20% conversion
**for runs "a" to "e" (122 days), GHSV=4300
***followed by H_2 at 204°C

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It can be seen that regeneration temperatures varied from 293 to 510°C. Regeneration at about 510°C resulted in decreased, and presumably irreversible, catalyst activity.

20 **V Effect of co-feeding water with hydrogen-deficient syngas**

Hydrogen deficient syngas ($H_2/CO<1$) as is produced by present day and some times preferred more economic gasifiers can be utilized to some considerable advantage by a selective conversion to dimethyl ether (DME) with appropriate synthesis catalysts. In such an operation, water can be co-fed along with low ratio syngas for contact with selected DME synthesis catalysts where by virtue of the
25 water-gas-shift activity of components of selected DME catalysts it is converted with a like amount of CO to hydrogen plus CO_2. Syngas utilization can be improved and/or the mole ratio of a H_2/CO effluent from the DME synthesis step upgraded in this manner as illustrated in the case of equilibrium conditions in Figures 1 and 2, referred to above.

The upgraded H_2/CO ratio gas recovered from the water co-fed DME synthesis step necessarily
30 contains other gases, principally CO_2. Because of the severe equilibrium penalty of such CO_2 diluent on DME conversion, utilization of this syngas may not be best effected by recycling this CO_2-containing gas to the DME synthesis step accompanied by the necessary purification of the recycled gas.

Recovered unreacted syngas streams, comprising appropriately upgraded H_2/CO ratio syngas, can alternatively be passed to conversion systems in which conversion activity is not equilibrium-
35 limited (as is the case of DME) and which can (perhaps with less selectivity) utilize the recovered unreacted syngas stream. A secondary reaction system particularly suitable for converting this CO_2-containing syngas comprises a Fischer–Tropsch conversion unit utilizing one of Fe-, Co- or Ru-type synthesis catalysts. Such a secondary synthesis catalyst system allows for optimum utilization of the recovered DME recycle syngas with minimal or no interstage CO_2 removal. Such a system is illustrated
40 in Figure 5, described above.

The upgraded syngas effluent from the DME sequence is particularly suited for subsequent utilization in a Fischer–Tropsch iron-based catalyst operation. In industrial and Engineering Chemistry—Process Research and Development, 15 (4) 1976, it is suggested that benefit is obtained from increasing both the H_2/CO feed ratio ($H_2/CO<6$) and the level of CO_2 at the F—T reactor entrance.
45 Decreasing the ratio of $(P_{co}/P_{H2})^3$ (i.e., increasing H_2/CO) decreases undesired carbon formation. Also selectivity of the hydrocarbon products to methane is decreased as P_{co2} increases. Thus benefit is received in the Fischer–Tropsch stage of a two-stage operation envisioned here when the H_2/CO ratio and the CO_2-content of the recovered interstage syngas stream are increased as a result of H_2O co-feed to the DME stage.

50 The syngas H_2/CO ratio recovered from or rejected by a DME unit as unreacted syngas when operating without water co-feed may not be sufficiently rich in hydrogen for use in the secondary unit. Upgrading can be accomplished in a separate water-gas-shift reaction unit—but is more economically achieved by co-feeding water with low ratio syngas passed to the DME synthesis unit. The specific secondary process comprising a F—T synthesis using Fe-, Co- or Ru-based catalysts will normally
55 require a 1 or higher H_2/CO mole ratio syngas such as provided by the effluent from the DME synthesis step. An understanding of the DME reactor synthesis behavior dictates the level of water to be charged with syngas obtained from the gasification step, as is illustrated below. Also the amount of water co-fed with the syngas should be constrained, as discussed below.

For syngas feeds of H_2/CO mole ratio, r, less than 1, water can be co-fed with this syngas to a
60 dimethyl ether synthesis reactor in amounts given by

$$\frac{r'-r}{1+r'} \leq S < 1$$

where S is the mole ratio of H_2O/CO and the stoichiometry parameter r' has an arbitrary value constrained by the relation of $r<r'\leq1$. The mole ratio of H_2/CO effluent from the reactor will increase as S is increased.

5   The limits on S can be expressed in terms of idealized behavior, as follows:

1) the upper limit on S, S<1, is established by the fact that, were complete shift of CO with H_2O to H_2 and CO_2 to occur, in the case of S=1, no CO would remain for subsequent ether synthesis.

2) the syngas stoichiometry parameter, r', has important significance. Dimethyl ether stoichiometry anticipates a molar feed ratio for H_2/CO of r'=1.0. When the molar feed ratio, r, is <1,

10   water co-fed in the molar amount

$$S=\frac{r'-r}{1+r'}=\frac{1-r}{2}$$

would yield an effective H_2/CO ratio of 1.0 if all co-fed H_2O were to shift completely with available CO to form H_2 and CO_2.

3) the lower limit on r' wherein r'<r expresses the requirement that the numerator of the left hand side of equation (4) be positive.

15   The limits and concepts discussed above are, of course, idealized—with their actual values depending on the complex equilibrium and dynamic behavior of a reactor with such factors as catalyst bypass and backmixing further complicating a priori predictions. For a specific reactor configuration and synthesis operating parameters, extensive variables such as syngas conversion or H_2/CO ratio at

20   the reactor exit can be correlated with the water co-feed parameter (S). With the aid of such correlations the desired S value in the range specified by equation (4) can be determined.

Such correlation is illustrated by the following sequence of tests.

Two further catalysts, XIV and XV, were prepared in two parts. First, a methanol component was prepared by co-precipitation of three metal components from an aqueous stirred solution of their

25   nitrates by the addition of excess hot (85—90°C) sodium carbonate solution. The resulting precipitate was washed, dried and calcined at about 260°C.

These methanol components were then ground to powders and each was combined with an equal part by weight of gamma-alumina powder (ground American Cyanamid SB #464).

Catalyst XIV had a methanol component prepared from equal amounts of copper, zinc and

30   chromium. Catalyst XV had a methanol component prepared from equal atom amounts of copper, zinc, and aluminum.

Both catalysts were initially activated by contacting at 1 atm. and 204°C with a hydrogen/inert gas stream whose hydrogen composition was slowly increased to 2 volume percent and then to 8.5 volume percent and then operated at synthesis conditions for extended periods with periodic oxidative

35   regeneration. These oxidative regenerations were carried out by purging the reactor with inert carrier; passing over the catalyst a pulse of oxygen of 100 liters STP/liter catalyst at atmospheric pressure, a temperature of 288 to 343°C and a space velocity sufficiently slow to prevent thermal damage of the catalyst; and then gradually displacing an inert purge stream at reaction conditions with syngas charge.

Catalyst XIV was operated with daily regeneration under the following nominal conditions:

40   316°C, 50—54 atm; GHSV (based on syngas)=1000; H_2/CO mole feed ratio=2/3 and at various levels of co-fed water. As indicated in Figure 3, the water co-feed level was varied throughout the period of the experiment. In Figure 4 the results of this experiment are correlated with the amount of water co-fed per unit amount of CO fed, S, for two variables—the reactor exit H_2/CO mole ratio (A) and the total syngas conversion in terms of H_2+CO reacted (B)—and the observed values are compared

45   with those projected for thermodynamic equilibrium conversions at appropriate feed conditions. Results such as those presented in Figure 4 can be obtained for the particular dimethyl ether synthesis system of interest.

Catalyst XV was contacted at 316°C with synthesis gas of H_2/CO mole ratio=2/3 for an extended period at a water co-feed level of 0.25 mole H_2O/CO and a pressure of 54 atmospheres and

50   periodically oxidatively regenerated. Catalyst behavior 18 hours after regeneration and after 30 days of contact is set out in Table 5. The effluent H_2/CO mole ratio of 0.85 indicates enrichment of the feed ratio. Comparisons of the observed effluent H_2/CO ratio and conversion for this run on Catalyst XV indicate a divergence from equilibrium similar to that correlated for Catalyst XIV.

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Table 5
Dimethyl ether synthesis products 18 hours after regeneration

	Catalyst XV
Feed	
H$_2$/CO	.67
H$_2$O/CO	0.25
Reaction Conditions	
DAYS OPR	30.0
T RXR °C	316
P ATM	54
GHSV	1200
WHSV	0.98
KG/L/HR	0.95
Reactor Product Distribution, (wt.%)	
H$_2$	1.9
CO	31.3
CO$_2$	45.5
H$_2$O	0.56
DME	19.3
CH$_3$OH	1.3
CH$_4$	0.10
C$_2$+	0.04
Conversions, (Mole%)	
H$_2$	52.2
CO	62.3
Total	58.3
Selectivites:	
D/(D+M)	98
Space Time Yields:	
KG/L/HR	0.195

In a final test, a tubular reactor was operated as a Fischer-Tropsch/iron system using a catalyst composed of the compressed powders of Fe$_3$O$_4$ and γ-alumina in a weight ratio of 1:10, respectively. The reaction conditions were: H$_2$/CO feed ratio=1/1; pressure (H$_2$+CO)=27 atmospheres; WHSV (based on H$_2$+CO to metal)=10.3; and temperature=320°C and the following results were obtained: H$_2$+CO conversion=89% hydrocarbon products distributed as methane 21%; C$_2$—C$_4$ 37%; and C$_5$+42% Similar results are to be expected if the feed to the reactor comprises syngas with a H$_2$/CO mole ratio of 1 and diluent CO$_2$, provided that the inlet H$_2$+CO partial pressure is maintained at a similar level (27 atmospheres).

The recovered, unreacted syngas effluent from the DME reaction system using Catalyst XIV described above can be adjusted to comprise H$_2$/CO of mole ratio 1 or higher by the co-feed of an appropriate amount of water. From Figure 4A, the water feed rate which results in an effluent H$_2$/CO mole ratio of 1 is projected to be 0.31 mole H$_2$/CO. Thus, in a specific example of a two-stage operation in accordance with this invention as illustrated in Figure 5, the Catalyst XIV is operated as described above with a feed H$_2$O/CO mole ratio of 0.31 thereby producing a dimethyl ether product with about 47% syngas conversion and a recovered effluent syngas stream with a H$_2$/CO mole ratio of about 1 which is suitable for use as a feed to a Fischer-Tropsch operation.

Claims

1. A process for converting synthesis gas into dimethyl ether which comprises contacting synthesis gas at a temperature of from 232 to 399°C with a catalyst composition of coprecipitated Cr, Cu and Zn components and of an acidic dehydrating component, in which the atomic ratio Cr/(Cu+Zn) is from 0.1 to 1.0, and subsequently regenerating the catalyst composition by contacting it with an oxygen-containing gas at a temperature of from 38 to 538°C.

2. A process according to claim 1, wherein the catalyst is regenerated at a temperature of from 288 to 454°C.

3. A process according to claim 1, wherein the catalyst is regenerated at a temperature of from 293 to 343°C.

4. A process according to any one of claims 1 to 3, wherein after regeneration, the catalyst is contacted with synthesis gas at a temperature of from 177 to 232°C and wherein the temperature is subsequently increased to the temperature of the conversion process.

5. A process according to any one of claims 1 to 3, wherein after regeneration, the catalyst is contacted with synthesis gas diluted with an inert gas at a temperature of from 177 to 232°C and wherein subsequently the temperature is raised and the concentration of the synthesis gas is increased to those of the conditions of the conversion process.

6. A process according to any one of claims 1 to 5, wherein the Cr/(Cu+Zn) atomic ratio of the catalyst composition is from 0.25 to 0.75 and the Cu/Zn atomic ratio is from 0.5 to 3.0.

7. A process according to any one of claims 1 to 6, wherein the acidic dehydrating component of the catalyst is gamma-alumina.

8. A process according to claim 7, wherein the gamma-alumina comprises 50% by weight of the catalyst composition.

9. A process according to any one of claims 1 to 8 wherein the coprecipitated catalyst components are prepared by carbonate-coprecipitation from a solution of the nitrates of the metals, washing the precipitate to remove carbonate, and calcining the washed precipitate in air at a temperature of about 260°C for a period exceeding about 6 hours.

10. A process according to any one of claims 1 to 9, wherein the synthesis gas feed has a H_2/CO molar ratio of from 0.5 to 3.0.

11. A process according to any one of claims 1 to 9, wherein the synthesis gas feed has a H_2/CO molar ratio of from 0.5 to 2.0.

12. A process according to any one of claims 1 to 9, wherein the synthesis gas feed has a H_2/CO molar ratio of from 0.5 to 1.

13. A process according to claim 12, wherein water is fed to the catalyst with the synthesis gas, the amount of water being sufficient to supplement the hydrogen deficiency of the synthesis gas.

14. A process according to claim 13, wherein the amount of water is from 0 to 50 moles per 100 moles of CO in the synthesis gas.

15. A process according to any one of claims 12 to 14, wherein synthesis gas having a H_2/CO mole ratio, r, less than 1 and water in an amount defined by the relationship

$$\frac{r'-r}{1+r'} \leq S < 1$$

in which S is the mole ratio H_2O/CO and r' is an arbitrary value constrained by $r < r' \leq 1$, are converted into a product comprising dimethyl ether and methanol.

16. A process according to claim 15, wherein r' is 1.0.

17. A process according to claim 15, wherein unreacted synthesis gas comprising CO_2 is separated from the dimethyl ether and methanol.

18. A process according to claims 15 to 17, wherein the unreacted synthesis gas has a higher H_2/CO ratio than the synthesis gas feed.

19. A process according to claim 18, wherein the unreacted synthesis gas has a H_2/CO mole ratio of at least 0.85.

20. A process according to claim 18, wherein the unreacted synthesis gas has a H_2/CO mole ratio of at least 1.0.

21. A process according to any one of claims 17 to 20, wherein the unreacted synthesis gas is contacted with a Fischer-Tropsch catalyst and converted into a product mixture of carbon-hydrogen compounds.

22. A process according to claim 21, wherein the Fischer-Tropsch catalyst comprises an Fe, Co or Ru component.

23. A process according to claim 22, wherein the catalyst also comprises a zeolite.

24. A process according to claim 23, wherein the zeolite is ZSM—5.